BIS-(p-3,5-DIOXO-1,2,4-TRIAZOLINE-4-YLPHENYL)-METHANE AND
IT'S REACTIONS WITH DIALLYL COMPOUNDS

By

Wayne Eugene Ruch

A THESIS PRESENTED TO THE GRADUATE COUNCIL OF THE
UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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Abstract of Thesis Presented to the Graduate Council of the
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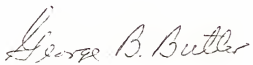IT'S REACTIONS WITH DIALLYL COMPOUNDS

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Wayne Eugene Ruch

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Chairman: Dr. G. B. Butler
Major Department: Chemistry

This thesis presents a method of catalytic preparation
of bis-(p-3,4-dioxo-1,2,4-triazoline-4-ylphenyl)-methane
and the subsequent formation of a new class of polymers by
the reaction of the bis compound and various diallyl com-
pounds.

Evidence is presented to support the theory that the
mechanism involved is a Diels-Alder-Ene mechanism.

George B. Butler
Chairman

CHAPTER I

INTRODUCTION

A. General Background

4-Phenyl-1,2,4-Triazoline-3,5-Dione,1, (PhTAD) was first synthesized by Thiele[1] in 1894 along with other members of the Triazoline-Dione family. These 4-substituted compounds were obtained by oxidizing the corresponding urazole, 2, with lead peroxide in cold, dilute sulfuric acid. Other oxidative methods used to date, have included treating the urazole with t-butyl hypochlorite in acetone,[2] lead tetraacetate in methylene chloride,[3] bromine,[4] fuming nitric acid in cold methylene chloride,[5] dinitrogen tetroxide gas in methylene chloride,[6] manganese dioxide, calcium hypochlorite or N-bromosuccinimide.[7]
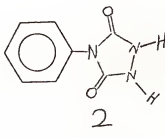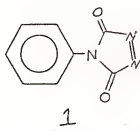

This author has found the most effective method to be the use of catalytic amounts of fuming nitric acid in methylene chloride at room temperature. Stirring inhibits

the reaction which also shows a short induction period.
Purification of the PhTAD is accomplished by evaporation of
the solvent and vacuum sublimation of the product.

Cookson, Gilani, and Stevens[2] recognized the potential
of PhTAD as a dienophile in Diels-Alder reactions. These
researchers reported that low temperature solutions of
PhTAD were stable in the absence of light and moisture, and
would react with cyclopentadiene and butadiene to give the
Diels-Alder adducts, 3, and 4, respectively.

$$\underline{3} \qquad\qquad \underline{4}$$
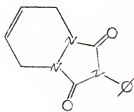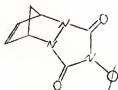
These results lead to the use of PhTAD to prepare
Diels-Alder adducts of various steroids.[8,9] During these
studies, it was noticed that PhTAD would react quickly
even where maleic anhydride would not react at all. Sauer[10]
has done kinetic studies which show PhTAD to be one of the
most powerful dienophiles existing. Evnin, Miller and
Evanega[11] report that a 1,4 cycloaddition product, 5, can
be formed from cyclooctatetraene and PhTAD even though this
reaction is not known to occur with other dienophiles. The
compound PhTAD was used to trap Dewar benzene to give 6,[12]
reacted with cyclononatetraene to give 7,[13] reacted with
various cyclopentadiene derivatives.[14,15] A 2:1 adduct of

$\underline{5}$ $\qquad$ $\underline{6}$ $\qquad$ $\underline{7}$
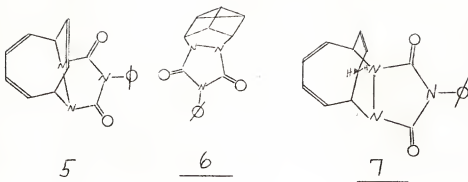
PhTAD with styrene can be formed by a double Diels-Alder reaction.[16] Reactions of PhTAD with vinyl compounds have been extensively studied.[17-20]

Dienophiles can also undergo the Diels-ene reaction which is similar to the Diels-Alder reaction. This mechanism is shown in Scheme I. A Diels-ene type of product was found in the reaction of PhTAD and the alkene (4-phenyl-butylidene)-cyclopropane.[21] Pirkle and Stickler[22] performed

SCHEME I
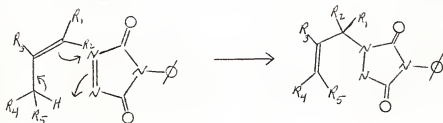
a series of kinetic studies and found PhTAD to be more than thirty thousand times as reactive as ethylazodicarboxylate with various monoolefins containing an α-hydrogen.

B. Research Objectives

The main objective of this study is to investigate the use of Triazoline-Diones in polymer formation.

Low molecular weight, alternating copolymers have been reported by Turner, Guilbault, and Butler[17] when vinyl ethers were reacted with Triazoline-Diones. Similar polymers were formed by the reaction of PhTAD with N-vinyl carbamates.[19]

Diels-Alder polymerization reactions are attractive, for they offer a method of producing ladder-type high-temperature polymers. However, few Diels-Alder reactions have been able to produce high molecular weight polymers. 2-vinylbutadiene undergoes a Diels-Alder self polymerization to form an insoluble compound,[23] while, 8, undergoes a Diels-Alder self polymerization in refluxing xylene to give a low molecular weight oil. Diels-Alder polymerizations involving

$$8 \qquad\qquad 9$$
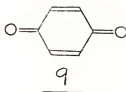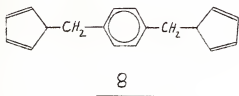
the reaction of bidienes, 10, with bidienophiles such as quinone, 9, or N,N'-bis(maleimide), 11, have been reported

$$10 \qquad\qquad 11$$
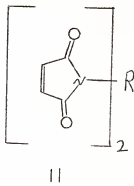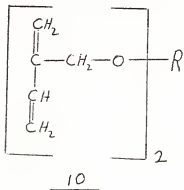
to give polymers of low intrinsic viscosity and softening points below 200° C.[24] Other bidienes, including 2-vinyl-butadiene,[24] 1,8-diphenyloctatetraene, 1,5-bis(9-anthryl)-1,4-pentadiene-3-one, and anthralazine[23] were used, but all gave only low molecular weight polymers. Reactions using bis(cyclopentadienyl) compounds as the bidiene were more successful,[25] but high molecular weight, linear polymers were still not obtained.
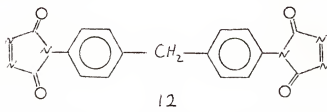
Bis-(p-3,5-dioxo-1,2,4-Triazoline-4-ylphenyl)-methane

12

(BDTD), 12, has been used by Saville[26] to crosslink natural rubber. The crosslinking was reported to have taken place by a Diels-ene reaction.

Reaction of BDTD, 12, with styrene was investigated by Turner,[27] who reported that a polymer was formed by a process which consisted of first a Diels-Alder reaction followed by a Diels-ene reaction on the product of the first reaction. This reaction was later investigated in depth by Wagener,[28] who confirmed the Diels-Alder-ene mechanism and determined that the reaction was giving a high molecular weight (η = 0.33 dl.g.) polymer. Wagener[29] also reacted BDTD with divinyl esters of dicarboxylic acids. BDTD and diisopropyl adipate gave some low molecular weight and a large amount of insoluble solid. BDTD and divinyl adipate gave an insoluble gel in tetrahydrofuran.

The high reactivity of triazoline-diones,[10] their ability to form high molecular weight polymers,[28] and the facility with which they undergo the Diels-ene reaction,[22] suggest the possibility that useful, high molecular weight copolymers may be prepared by the reaction of BDTD with various diallyl compounds.

CHAPTER II

RESULTS AND DISCUSSION

A. Formation of Diels-Ene Copolymers

Previous Results

Cookson, Gilani and Steves[16] reported that a double
Diels-Alder product, 13, was formed by the reaction of PhTAD
and styrene. Wagener,[30] investigating a reaction reported
by Turner,[27] showed that this product was actually a mixture
of a double Diels-Alder adduct and a Diels-Alder-ene adduct,
14, with the latter being formed in twice the amount of the

_13_   _14_
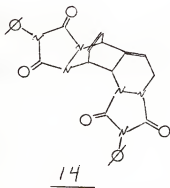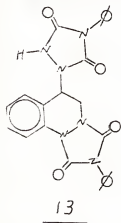
former. The reaction was repeated with 4-Methyl-1,2,4-
triazoline-dione, 15, which gave the same product ratio of
2:1 in favor of the Diels-Alder-ene adduct. The mechanism
suggested by Wagener,[20] an elaboration of the mechanism of
Turner,[27] is found in Scheme II.

SCHEME II
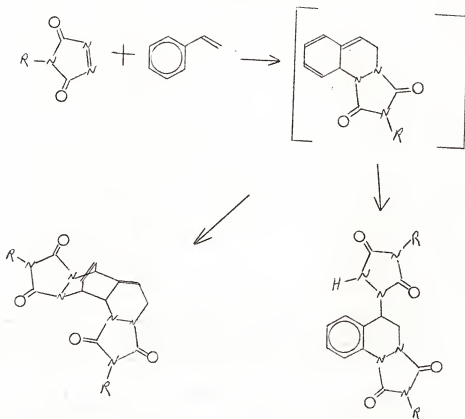
The formation of a double addition product by reaction of PhTAD with styrene suggests the possibility of formation of a copolymer by reacting BDTD, 12, with styrene. This reaction was performed by Turner,[27] who reported the formation of a copolymer whose nuclear magnetic resonance spectrum gave evidence of a Diels-Alder-ene type of structure, 16. This reaction was studied in more detail by Wagener,[28] who reported that reaction of concentrated solutions of BDTD in dimethyl formamide, when added to an equimolar amount of styrene, gave a high molecular weight copolymer. This

copolymer was found to consist of a mixture of Diels-Alder-
ene repeat units, 16, and double Diels-Alder repeat units,
17.

16

17

Styrene was also copolymerized with 1,6-hexane-bis-1,2,4-
Triazoline-dione, 18, which yielded a low molecular weight

18

of 2300.[20] The nuclear magnetic resonance spectrum for this
polymer indicated that the Diels-Alder-ene unit was present
in twice the amount of the double Diels-Alder unit.

B. Formation of New Copolymers

The BDTD used in this study was prepared by a modifi-
cation of the method used by Saville.[26]

One mole of bis-(4-isocyanatophenyl)methane,19, was
reacted with two moles of ethyl carbazate,20, to give the
bis-semicarbazide,21. The bis-semicarbazide was cyclized
by dissolving it in a 2M solution of potassium hydroxide,
and then neutralizing the resulting solution with hydro-
chloric acid to give the bis-urazole,22. The bis-urazole
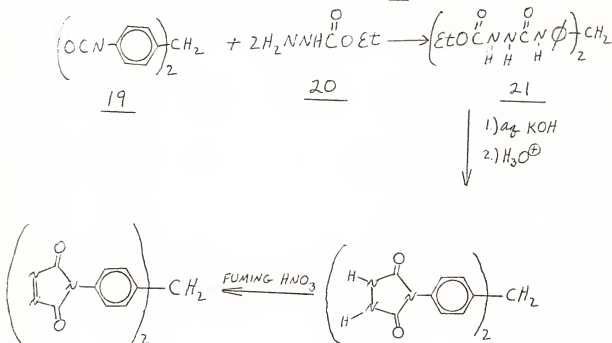
was then oxidized to form the bis-Triazoline-dione,23, by
either of two methods. During the early stages of these

studies, the urazole was oxidized by bubbling N_2O_4 gas
through a stirred slurry of the urazole in methylene chloride
at room temperature. As the oxidized product, 23, was formed,
it dissolved in the methylene chloride solvent to give a
bright red solution which is characteristic of Triazoline-
diones. During the latter part of these studies, it was
discovered that the reaction time could be shortened consid-
erably if fuming nitric acid was substituted for the N_2O_4
gas, and if the reaction mixture was not stirred. Only
catalytic amounts of the fuming nitric acid are necessary
for oxidation to take place. Amounts used were typically
on the order of five drops of fuming nitric acid for each
gram of the urazole to be oxidized. Since the bis-Triazoline-
dione was decomposed slowly by the moisture in the air, while
the urazole was unaffected, the compound was stored as the
urazole and the required amount oxidized to Triazoline-dione
immediately prior to use. The product formed by either
method of oxidation was shown to be the same compound by
infrared, nuclear magnetic resonance and elemental analysis.

The bis-Triazoline-dione is very soluble in polar sol-
vents to give bright red solutions, but decomposes in two
hours in dimethyl sulfoxide, one hour in dimethyl-formamide,
and decomposes in one and one-half hours with formation of
a tan precipitate in tetrahydrofuran. It is also decomposed
in less than fifteen minutes by wet acetone. The bis-
Triazoline-dione was found to be stable for over forty-

eight hours when dissolved in a 50/50 mixture of reagent
grade acetone and ethyl acetate, thus all reactions involving
BDTD were carried out in this solvent mixture.

Since PhTAD undergoes the Diels-ene reaction readily
with the allyl system,[21,22] the possibility was suggested
for the formation of copolymers by reacting BDTD, which also
forms compounds by the Diels-ene pathway,[28] with compounds
that contain more than one allyl group. To investigate this
possibility, BDTD was reacted with 1,6-heptadiene,24, diallyl
ether,25, triallylamine,26, diallylpropylamine,27, diallyl-
dimethylsilane,28, diallylmethylphenylsilane,29, diallyldi-
phenylsilane,30, and 2,6-diallyl-3,5-dimethoxyphenol,31.
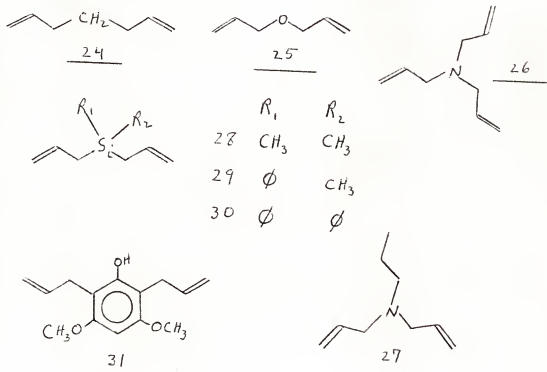
The heptadiene,24, and the ether,25, both reacted slowly,
taking over twenty-four hours to decolorize an equimolar

concentration of BDTD. The two amines, 26, and, 27, react
instantaneously with an equimolar concentration of BDTD in
acetone/ethyl acetate to form a thick white, insoluble pre-
cipitate. The diallylphenol, 31, took nineteen hours to
react. The ether, 25, the amines, 26, and, 27, and the phenol,
31, gave products in the form of white solids which were
insoluble in dimethylformamide, dimethyl sulfoxide, dichloro-
methane, acetone, ether, benzene, hexane, and chloroform.
These products could also be heated to 300° C. with no ap-
parent effects. The heptadiene, 24, also gave an insoluble
product that would not melt below 300° C., but would soften
at 287° C. Infrared spectra of these compounds indicated
that they were copolymers of BDTD with the diallyl compounds
and not a homopolymer of BDTD, a portion of which could be
recovered in each case. It appears that the BDTD unit is
capable of conferring a high degree of thermal stability to
the copolymers that it forms.

Since all of the BDTD copolymers were insoluble, model
compounds were prepared to be used in nuclear magnetic reso-
nance studies to help determine the structure of the copoly-
mers. This was done for all of the diallyl compounds men-
tioned above, except for the diallylphenol and the triallyl-
amine, by reacting them with two equivalents of PhTAD. The
products of these reactions, 32, 33, and, 34, were readily
purified by crystallization from chloroform, and soluble in
solvents such as acetone and dichloromethane. Mass spectra,
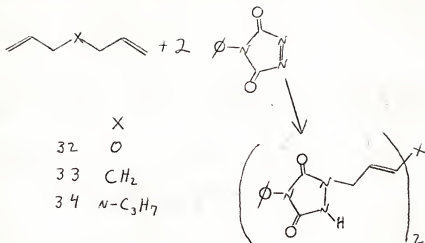
infrared spectra, nuclear magnetic spectra, and elemental
analysis indicated that the compounds, 32, 33, and, 34, were
2:1 adducts formed by a Diels-ene reaction of PhTAD on each
of the allyl groups. An adduct was not obtained in the re-
action of PhTAD with 2,6-diallyl-3,5-dimethoxyphenol, 31, be-
cause the PhTAD was decomposed by the presence of the hydroxyl
group. This was confirmed by the reaction of PhTAD with 3,5-
dimethoxyphenol, 35, which gave immediate decolorization of
the PhTAD solution. BDTD however, shows no change when added

35
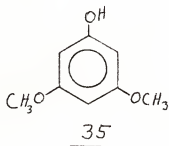
to a solution of three equivalents of 3,5-dimethoxyphenol
dissolved in a 50/50 mixture of acetone and ethyl acetate,
and allowed to sit for forty-eight hours.

Since BDTD should undergo the same Diels-ene reaction
that PhTAD does, the repeat units in the copolymers should

have structures that are analagous to the corresponding model compounds.
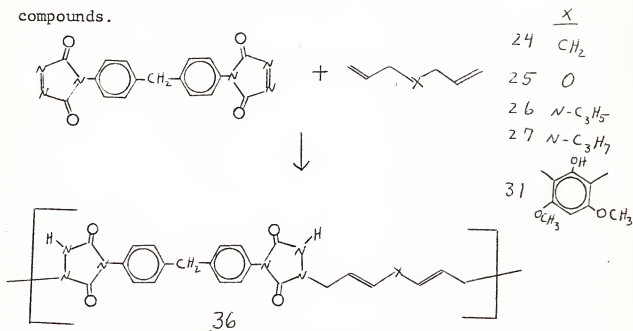
Cross-linking may be expected by reaction of the Triazoline-dione unit with the vinyl structure formed in the copolymer, 36, by the Diels-ene reaction, since studies by Turner, Guilbault, and Butler,[18] and by Wagener,[20] show that both PhTAD and BDTD react readily with a series of vinyl compounds. This type of cross-linking probably does not occur in the copolymers, for the compound, 37, can be allowed

37
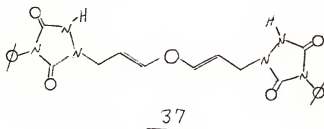
to sit for forty-eight hours in a solution of PhTAD dissolved in methylene chloride with no change in the elemental analysis of the recovered adduct, 37, or in the nuclear magnetic resonance spectrum.

The reactions of BDTD with the silicon compounds, 28, 29, and, 30, did not produce insoluble precipitates as did the other diallyl compounds. Instead, these compounds reacted to give an insoluble film which covered the inside of the reaction vessel. All the films produced were insoluble in dimethyl sulfoxide, dimethylformamide, acetone, ethyl acetate, methylene chloride, chloroform, ether, and hexane. They were partially soluble in a solution made by dissolving chromic acid in concentrated sulfuric acid. The films did differ in their mechanical properties. The film produced by the reaction of BDTD, 12, and diallyldimethyl-silane, 28, was opaque and could be lifted off the glass surface of the reaction vessel in the form of rubbery sheets, which were flexible but had a very low shear strength. This compound had a softening point of 204° C. and turned a transparent, dark red color at 270° C. This decomposition product was very hard and upon subsequent heating to 300° C. showed no further change. The films formed by the reaction of BDTD with diallylmethylphenylsilane, 29, and of BDTD with diallyl-diphenylsilane, 30, were both a transparent gold color. Both of these films were strong and inflexible. They also adhered strongly to the glass of the reaction vessel and could not be removed as sheets as in the case of the diallyldi-methyl copolymer, but instead had to be chipped off. The hardness of these films was approximately that of ice of the same thickness. The thickness of the polymer coating

was measured as being between 0.5 mm and 1.0 mm for both compounds. The two copolymers do differ in their thermal properties. The product of BDTD and diallylmethylphenyl-silane, 29, softened at 255° C. and then decomposed to the transparent red compound described earlier at 270° C., while the product of BDTD and diallyldiphenylsilane, 30, softened at 262° C. and decomposed at 270° C. to the same transparent red compound.

The rates of reaction of the silicon compounds, 28, 29, and, 30, with BDTD showed a progression. Diallyldimethyl-silane, 28, reacted the fastest, taking one hour to decolor-ize a solution containing one equivalent of BDTD. Diallyl-methylphenylsilane gave the next fastest rate, taking three hours to decolorize one equivalent of BDTD, while diallyl-diphenylsilane gave the slowest reaction, taking four hours to decolorize the BDTD solution. This progression of rates is probably due to the added steric hindrance of the phenyl group compared to the methyl group.

There is a soluble product left in the acetone/ethyl acetate solvent in each of the reactions of BDTD with the silicone compounds. This product can be recovered by drip-ping the acetone/ethyl acetate solution into a ten-fold ex-cess of hexane. In each case, this process gives a dis-persion in which the droplets adhere to any surface present in the flask and cover the surface with a yellow film. These films are soluble in polar solvents and can be crys-

tallized from chloroform to give bright yellow crystals.
These crystals showed the same changes in their physical
properties with increasing temperature as did the corres-
ponding insoluble compounds. The soluble fractions had the
same infrared spectra and elemental analysis as did the
corresponding insoluble compounds, thus they can be charact-
erized as being the low molecular weight fractions of the
insoluble polymers. Nuclear magnetic resonance spectra
were taken of these soluble compounds, and they, along with
the infrared spectra and elemental analysis of the insoluble
films, support the presence of repeat units formed by a 1:1
Diels-ene reaction between the triazoline-dione units on
BDTD with the allyl groups of the silane compounds.

	R_1	R_2
28	CH_3	CH_3
29	$\emptyset$	CH_3
30	$\emptyset$	$\emptyset$
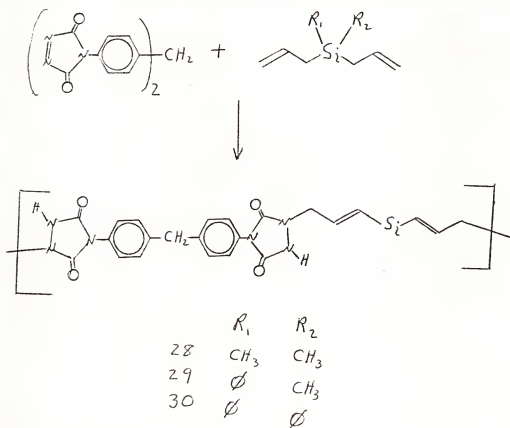
C. Reaction of PhTAD with Diallydialkylsilanes

PhTAD, 1, was reacted with diallyldimethylsilane, 28, diallylmethylphenylsilane, 29, and with diallyldiphenyl-silane, 30. These reactions showed a progression of rates with the dimethyl compound, 28, and the methylphenyl compound, 29, decolorizing a solution of two equivalents of PhTAD in methylene chloride, in less than five minutes. The diphenyl compound, 30, required two hours and fifteen minutes to decolorize the same PhTAD solution. This was to be expected after the results of the reactions of these same silicon compounds with BDTD. Once again the steric hinderance of the two phenyl groups slows the reaction rate.

The products of these reactions with PhTAD were re-covered by dripping the reaction mixture into a ten-fold excess of hexane with stirring. This procedure resulted in the form of a precipitate obtained from each mixture. These precipitates were then filtered, dried and recrys-tallized from chloroform. The crystallization gave bright yellow, granular crystals in each case. The results of elemental analysis and nuclear magnetic resonance spectra, did not agree with the expected structure, 38.

38
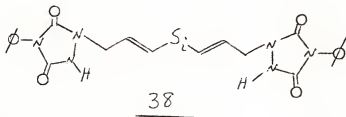
A sample of all three compounds was submitted for mass spectral analysis, and the resulting spectra indicated a cyclic structure, 39, from the molecular weights and the splitting patterns. This cyclic structure agrees with the

R_1	R_2
CH_3	CH_3
$\emptyset$	CH_3
$\emptyset$	$\emptyset$

39
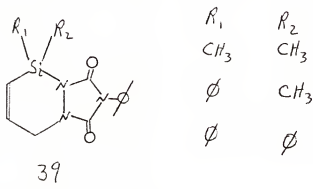
results of the elemental analysis and the nuclear magnetic resonance spectra.

Reaction of PhTAD with allyltrimethylsilane, 40, gave a product, 41, whose elemental analysis indicated it to be a 1:1 adduct as was expected. However, the nuclear magnetic resonance spectra of this compound shows the unambiguous pattern of an allyl group that is no longer attached to the silicon atom. The structure, 41, was assigned to this

41
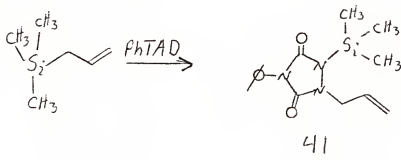
compound. This structure is supported by the splitting patterns found in the mass spectrum of this compound.

This compound is not cyclic, but the structure infers that there was either a cyclic transition state or a cyclic intermediate involved in its formation. A possible transition state is the six center transition state of the

41
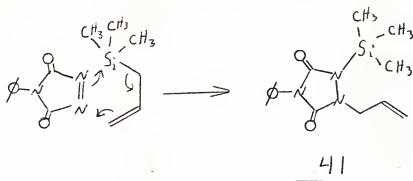
Diels-ene reaction, except in this case an Si atom is abstracted instead of an H atom. This reaction is probably facilitated by the possible interaction of the non-bonding electrons of the nitrogen with the empty d-orbitals of the silicon. Because of these d-orbitals, the mechanism might not be concerted, but may rather involve an intermediate, 42,

42   41
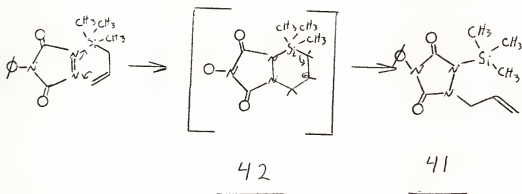
in which loss of the Si from the carbonium ion would be preferred to loss of a proton.

Application of this second possibility to the reaction of PhTAD with the diallyldialkylsilane compounds, yields a tentative mechanism for the formation of the products observed. This mechanism is shown in Scheme III.

SCHEME III

R_1	R_2
CH_3	CH_3
$\emptyset$	CH_3
$\emptyset$	$\emptyset$
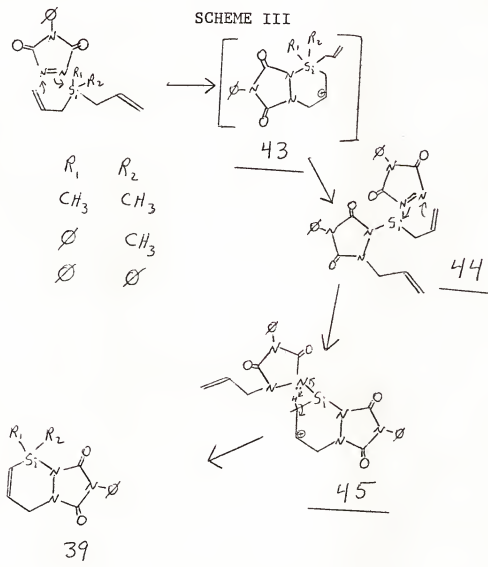
The second intermediate, 45, does not break the carbon-silicon bond as would happen in the first intermediate, 43,

for the nitrogen introduced in the first step is in a position where the non-bonding electrons can help abstract a proton to form the double bond. At the same time the proton transforms the triazoline-dione unit into a good leaving group to regenerate the tetravalent silicon.

The cyclic product, 39, could still be formed if the intermediate product, 44, should undergo a normal Diels-ene reaction between the allyl group of the silicon and PhTAD to give the intermediate product, 46. This is shown in Scheme IV.

SCHEME IV
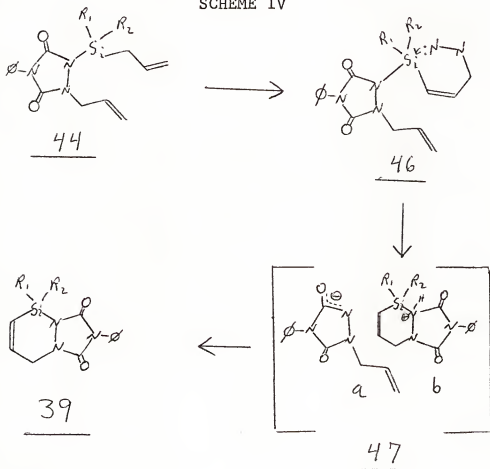
The nitrogen of the newly added triazoline-dione unit could attack the silicon in an S_n2 manner to replace the triazoline-dione unit already bonded to the silicon atom to give,_47_. The unstable intermediate,_47_, could then form the final cyclic product,_39_, by loss of a proton. Silicon is known to be a center of attack for nucleophilic substitution reaction,[31] and the negative charge of the leaving triazoline-dione unit could be somewhat stabilized by resonance with the oxygen of the adjacent carbonyl group,_47a_.

D. Reaction of PhTAD with Acetone

In purifying some of the previously mentioned PhTAD adducts formed in 50/50 acetone-ethyl acetate solvent, a very soluble low molecular weight contaminant was found, whose increase in yield was directly proportional to the decrease in rate of the main reaction. The same compound could be obtained in high yield by allowing solutions of PhTAD in both 50/50 acetone-ethyl acetate and in dried acetone to sit until decolorization of the solution had occurred. The product could not be obtained from PhTAD in ethyl acetate. The product was an adduct of PhTAD and acetone, which formed in a very slow reaction. This compound was recovered by dripping the decolorized solution into a ten-fold excess of hexane. This resulted in a yellow oil which was purified by dissolving in methylene chloride and allowing crystals to grow. These crystals were bright yellow color and had a melting range of $126^{\circ} - 127^{\circ}$ C. The

nuclear magnetic resonance spectra of this compound, 48, gave
two sharp singlets at τ = 7.9 and τ = 5.6, and a multiplet
in the aromatic region at τ = 2.5. These peaks had proton
ratios of 3:3:5 respectively. Mass spectral splitting pat-
terns, infrared spectra, and elemental analysis agree with
the structure assigned, 48. A mechanism can be written for
this reaction of PhTAD with the enol form of the acetone
molecule, 49, which has the six center transition state com-
mon to the Diels-ene reaction.
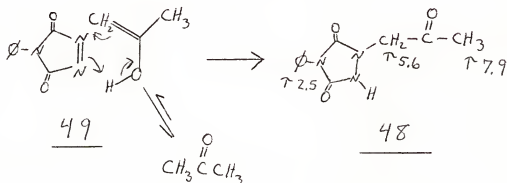
The slow rate of the reaction is due to the low concentration
of the enol form. This reaction suggests the possibility
of polymer formation between BDTD and the correct diketones.

Cookson, Gilani and Stevens[16] reported formation of
this compound, 1-acetonyl-4-phenyl-1,2,4-triazoline-3,5-
dione, m.p. 134 - 136°, in a similar manner; however, these
authors did not suggest a mechanism for its formation.

CHAPTER III

EXPERIMENTAL

A. General Information

Nuclear magnetic spectra were taken on a Varian A-60 spectrometer and infrared spectra were taken on a Beckman IR-8 spectrophotometer. Mass spectra were taken on a Model MS-30 mass spectrometer.

Melting points were taken on a Fisher-Johns melting point apparatus and are reported in degrees centigrade uncorrected.

Elemental analysis were completed by Atlantic Microlab Inc., of Atlanta, Georgia.

All reagents used were obtained commercially and used as received except as noted. All solvents were commercial grade and used as received.

B. Synthesis of 4-Phenyl-1,2,4-Triazoline-3,5-Dione

Ethyl Carbazate[3]

Diethyl carbonate (1.80 mol., 200.0 g.) and 99% hydrazine hydrate (1.80 mol., 88.0 g.) were mixed together with continuous stirring for thirty minutes. This resulted in an exothermic reaction in which the two phases initially

present combined to form one phase. The product of this reaction was distilled twice at 95° C. and 12 mm. This gave a yield of 130 g. (74%) of a white solid, mp 45-46° (Lit.[4] 44-45.5°).

1-Ethoxycarbonyl-4-phenylsemicarbizide[32]

Ethyl carbazate (0.62 mol., 60.0 g.) was dissolved in 200 ml benzene and cooled to 10° C. in a three-neck, 500 ml, round bottom flask fitted with an addition funnel, a mechanical stirrer, and a reflux condenser with a drying tube. Phenyl isocyanate (0.62 mol., 57.3 g.) was added dropwise through the addition funnel with stirring. This resulted in the formation of a white precipitate. After the addition was completed, the cold bath was removed and the mixture was refluxed for one half hour, during which time the white precipitate dissolved. When the solution was cooled to room temperature, the white precipitate reformed. This precipitate was filtered and washed twice with 75 ml portions of cold benzene. The yield was 108.6 g. (89.9%) of a white solid with a melting point of 153° C (Lit.[32] 154°).

4-Phenyl Urazole

1-Ethoxycarbonyl-4-phenylsemicarbazide (0.55 mol., 124.0 g.) was dissolved in 300 ml of hot 4M potassium hydroxide with stirring. The resulting light yellow solution was filtered and cooled. The solution was cooled in an ice-bath

and acidified with 6M hydrochloric acid to give a large amount of white precipitate. The precipitate was collected by filtration and washed with enough cold water to remove any traces of acid. The washed precipitate was dried over-night in a vacuum oven yielding 71 g. (80.4%) of a white solid, mp 205-207° C (Lit.[32] 206-207° C).

4-Phenyl-1,2,4-Triazoline-3,5-Dione

4-Phenyl urazole (3.43 x 10^{-2} mol., 6.0 g.) was placed in a 500 ml erlenmeyer flask with 100 ml dichloromethane. This mixture was allowed to sit unstirred at room temperature while 4 drops of fuming nitric acid was added. There was a short induction period, after which the white urazole turned red and dissolved in the dichloromethane to give a red solution. The dichloromethane solution was filtered and evaporated by blowing a stream of compressed air over the surface of the solution. This resulted in a bright red crystalline substance which sublimed at 80° C and 1.0 mm. This material was used immediately upon preparation. Yield 5.6 g. (95.5%).

C. Synthesis of Bis-(p-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)-methane[26]

Bis-(4-isocyanatophenyl) methane was purified by vacuum distillation to give a clear colorless liquid which solidified on standing to white needle crystals. The

isocyanate (61.7 g., .247 mol.) was dissolved in 300 ml
benzene. The resulting solution was added dropwise to a
solution of ethyl carbazate (51.4 g., .494 mol.) dissolved
in 200 ml benzene and cooled sufficiently to keep the re-
action temperature between 5° and 10° C. After the addition
was completed, the solution was allowed to warm to room
temperature. This resulted in a large amount of white pre-
cipitate which was filtered out and washed twice with cold
100 ml portions of benzene. The white precipitate was placed
in a vacuum oven to dry overnight. This gave a white powder,
mp 239-242° C (Lit.[26] 240-244° C). Yield 101 g. (91.2%).

The bis-semicarbazide formed above (.22 mol., 101 g.)
was dissolved in 500 ml 4M potassium hydroxide with stirring
and heating to give a yellow-green solution. The solution
was cooled to room temperature and acidified with 6M hydro-
chloric acid. This gave a large amount of white precipitate
which was filtered out of the solution and washed with cold
water. The washed precipitate was left in a vacuum oven to
dry overnight. This gave a 94 g. (92.2%) yield of the bis-
urazole with mp 318° (Lit.[26] 320°).

The bis-urazole (4 g., .011 mol) was placed in a 50 ml
erlenmeyer with 25 ml dichloromethane. This mixture was
allowed to sit unstirred at room temperature while 4 drops
of fuming nitric acid were added. This resulted in a re-
action which formed a red solution. The dichloromethane
was evaporated by blowing a stream of compressed air over

the surface of the liquid. This gave 5.2 g. (87%) of the
bright red bis-triazoline-dione which decomposed at 326° C
(Lit.[26] 320°).

> Anal. Calc. $C_{17}H_{10}N_6O_4$; C, 56.36; H, 2.98; N, 23.20
>
> Found: C, 56.28; H, 3.01; N, 23.33

D. Synthesis of New Copolymers

Reaction of BDTD with 1,6-heptadiene

BDTD (1.00 g., 2.77 x 10^{-3} mol.) was dissolved in 30 ml
50/50 ethyl acetate/acetone cosolvent at room temperature.
To the bright red solution which formed, 1.6-heptadiene
(.266 g., 2.77 x 10^{-3} mol.) was added dropwise with stirring.
There was no immediate color change observed. After two
hours the solution had become orange in color, and was ob-
served to be cloudy. 24 hours after the addition, there
was a yellow layer of solid material covering the bottom of
the reaction vessel. This solid was isolated, washed with
dichloromethane, and dried. After drying, the solid was
observed to be brittle, and could be easily crushed to a
yellow powder. This solid would not melt below 300° C,
but would soften at 287° C. Infrared absorbances were ob-
served (KBr) 3500 (m,b), 3300 (m), 2980 (w), 1800 (m), 1730
(s,b), 1670 (w), 1600 (w), 1500 (m), 1430 (m), 1200 (w),
1000 (w), 970 (m), 760 (w) cm^{-1}.

> Anal. Calcd. for 1:1 copolymer $C_{24}H_{21}N_6O_4$: C, 63.03;
> H, 4.59; N, 18.37.
>
> Found: C, 63.92; H, 4.48; N, 18.28.

Reaction of BDTD with Diallyl Ether

BDTD (1.00 g., 2.77 x 10^{-3} mol.) was dissolved in 20 ml 50/50 ethyl acetate/acetone cosolvent at room temperature. Diallyl ether (.271 g., 2.77 x 10^{-3} mol.) dissolved in 10 ml 50/50 ethyl acetate/acetone, was added dropwise with stirring. After 43 hours, the reaction mixture was still a pale pink in color and had a heavy suspension of pink particles. These particles were so fine that they would pass through a medium glass frit and completely clog a fine glass frit. It was discovered that upon addition of 25 ml hexane, the particles would clump together and could be filtered with a coarse glass frit. After washing with acetone and drying, a white powder (1.12 g., 88% yield) was obtained. This compound was heated to 300° C. with no visible change. Infrared absorbances were found at (KBr) 3500 (m), 3300 (m), 2990 (w), 1800 (m), 1730 (s), 1640 (s), 1610 (s), 1600 (m), 1510 (m), 1440 (m), 1290 (s), 1200 (w), 1000 (w), 760 (w) cm^{-1}.

Anal. Calcd. for 1:1 copolymer $C_{23}H_{19}N_6O_5$ C, 60.15; H, 4.14; N, 18.29.

Found: C, 60.23; H, 4.08; N, 18.36.

Reaction of BDTD with Diallylpropylamine

BDTD (1.00 g., 2.77 x 10^{-3} mol.) was dissolved in 20 ml 50/50 ethyl acetate/acetone. To this, a solution of diallyl-propylamine (.377 g., 2.77 x 10^{-3} mol.) in 10 ml 50/50 ethyl acetate/acetone, was added dropwise with stirring. The reaction was instantaneous, resulting in decolorization of

the red BDTD solution and formation of a heavy, white pre-
cipitate. Yield of white powder after washing and drying
was 1.31. g. (92.4%). This powder could be heated to 300° C.
with no visual change. Infrared absorbances were found at
(KBr) 3500 (m), 3350 (m), 3000 (w), 1810 (m), 1740 (s),
1600 (w), 1500 (m), 1440 (m), 1300 (s), 1220 (s), 1200 (m),
1160 (m), 1050 (m), 1000 (w), 770 (w).

Anal. Calcd. for 1:1 copolymer $C_{26}H_{26}N_7O_4$ C, 62.42:
H, 5.20: N, 19.59: O, 12.79.

Found: C, 62.54; H, 5.28; N, 19.73.

Reaction of BDTD with Triallylamine

BDTD (1.5 g., 4.66 x 10^{-3} mol.) was dissolved in 30 ml
50/50 ethyl acetate/acetone. To this was added triallylamine
(.377 g., 2.77 x 10^{-3} mol.) dissolved in 10 ml 50/50 ethyl
acetate/acetone. The amine solution was added dropwise
with stirring at room temperature. This resulted in instant-
aneous decolorization of the red BDTD solution and immediate
formation of a white clump of solid material. This clump
had the consistency of dried mud while still under the sol-
vent and could be crushed easily with a stirring rod to a
white powder. After washing with acetone and drying, the
yield was 1.83 g., 95.7%. This material would darken at
224° C, but still had not softened at 300° C. Infrared
absorbances were found at (KBr) 3500 (m), 3250 (m), 3000
(w), 1800 (m), 1730 (s), 1600 (w), 1500 (m), 1420 (m),

1360 (s), 1280 (s), 1200 (w), 1100 (m), 1020 (w), 750 (w).

$\underline{Anal.}$ Calcd. for 1:1 copolymer $C_{36}H_{33}N_{10}O_6$: C, 61.64; H, 4.71; N, 19.96; O, 13.69.

Found: C, 61.70; H, 4.56; N, 20.13.

Reaction of BDTD with 2,6-diallyl-3,5-dimethoxyphenol

BDTD (1.00 g., 2.77 x 10^{-3} mol.) was dissolved in 20 ml 50/50 ethyl acetate/acetone. 2,6-diallyl-3,5-dimethoxy-phenol (.651 g., 2.77 x 10^{-3} mol.) was dissolved in 10 ml 50/50 ethyl acetate/acetone, and this was added dropwise to the BDTD solution with stirring at room temperature. After a reaction time of nineteen hours, the solution had changed from a bright red color to a pale yellow color with a waxy white substance covering the bottom of the flask. This material was isolated by decanting the liquid of, adding fresh acetone and grinding the material under acetone. This procedure was repeated twice with 15 ml portions of acetone and one 15 ml portion of dichloromethane. This treatment turned the white wax to a white powder, which was allowed to air dry. Yield 1.06 g. (64.2%). This powder was heated to 300° C. with no visible change. Infrared absorbances were found at (KBr) 3600 (w), 3300 (m), 2980 (w), 2850 (s), 1950 (m), 1810 (m), 1730 (s), 1640 (s), 1620 (s), 1590 (m), 1500 (m), 1430 (m), 1410 (m), 1200 (w), 1000 (w), 840 (m), 760 (w) cm^{-1}.

$\underline{Anal.}$ Calcd. for 1:1 copolymer: $C_{31}H_{27}N_6O_7$: C, 62.54;

H, 4.53; N, 14.11; O, 18.81.

Found: C, 62.35; H, 4.59; N, 14.34.

Reaction of BDTD with Diallyldimethylsilane

Diallyldimethylsilane (.388 g., 2.77 x 10^{-3} mol.) was
weighed into a flask containing 10 ml 50/50 ethyl acetate/
acetone. To this solution, another solution consisting of
BDTD (1.00 g., 2.77 x 10^{-3} mol.) dissolved in 20 ml 50/50
ethyl acetate/acetone was added dropwise, at room temper-
ature with stirring. Midway through the addition, the re-
action mixture was red in color, but had started to turn
opaque. One hour after the addition had been completed,
the mixture had turned a light golden yellow and a film was
observed covering the entire inside surface of the reaction
vessel up to the solvent level. The solvent was decanted
off and the film allowed to dry. The film was opaque and
did not adhere to the reaction vessel, instead it could be
stripped off in flexible sheets. These sheets were insol-
uble in all solvents tried and only partially soluble in
C O_3/H_2SO_4. The film was washed in acetone and dried.
Yield 1.15 g (83.0%). Softened at 204° C., turned dark red
at 270° and showed no further change at 300° C. Infrared
absorbances were found at (KBr) 3500 (m), 3330 (m), 3000 (w),
1800 (m), 1750 (m) 1670 (w), 1500 (m), 1410 (m), 1260 (s),
1200 (m), 1000 (w), 950 (m), 840 (s), 760 (w) cm^{-1}.

Anal. Calcd. for 1:1 copolymer $C_{25}H_{25}N_6O_4Si$: C,

59.89; H, 4.99; N, 16.75; O, 12.76; Si, 5.60.

Found: C, 59.84; H, 5.01; N, 16.40.

Reaction of BDTD with Diallylmethylphenylsilane

Diallylmethylphenylsilane (.560 g., 2.77 x 10^{-3} m)
was weighed into a flask containing 10 ml. 50/50 ethyl
acetate/acetone. To this solution another solution con-
taining BDTD (1.00 g., 2.77 x 10^{-3} m) dissolved in 20 ml
50/50 ethyl acetate/acetone was added dropwise with stir-
ring. One hour after addition the mixture was still red,
but a film could be seen growing on the side of the reaction
vessel. After six hours the solvent was poured off and the
film allowed to air dry. After drying this film was found
to adhere strongly to the glass vessel, but could be chipped
off. Yield 1.35 g. (86.6%). Infrared absorbances were
found at (KBr) 3500 (m), 3300 (m), 3000 (w), 1820 (m), 1750
(m), 1670 (m), 1630 (m), 1490 (m), 1430 (m), 1260 (s), 1200
(w), 1130 (s), 1000 (w) 970 (m), 830 (s), 760 (w) cm^{-1}.

Anal. Calcd. for 1:1 copolymer $C_{29}H_{27}N_6O_4Si$: C,
63.17; H, 4.90; N, 15.20; O, 11.6; Si, 5.09.

Found: C, 63.22; H, 4.87; N, 15.37.

Reaction of BDTD with Diallyldiphenylsilane

Diallyldiphenylsilane (.731 g., 2.77 x 10^{-3} mol.) was
weighed into a flask containing 10 ml 50/50 ethyl acetate/
acetone. To this solution, another solution consisting of
BDTD (1.00 g., 2.77 x 10^{-3} mol.) dissolved in 20 ml 50/50

ethyl acetate/acetone was added dropwise with stirring at room temperature. A film was noticed on the sides of the flask but its growth was much slower than with the other two diallylsilanes. After six hours the solvent was poured off and the film allowed to air dry. This film adhered strongly to the sides and bottom of the flask. Yield 1.47 g (84.9%). M.P.: Softens 262° C., decomposes 270°C. Infrared absorbances were found at (KBr) 3500 (m), 3300 (m), 2980 (w), 1810 (m), 1730 (s), 1600 (m), 1630 (s), 1510 (m), 1430 (m), 1220 (m), 1125 (s), 1000 (w), 970 (m), 750 (w).

Anal. Calcd. for 1:1 copolymer $C_{34}H_{29}N_6O_4Si$: C, 66.56; H, 4.75; N, 13.69; O, 10.4; Si, 4.58.

Found: C, 66.43; H, 4.70; N, 13.79.

E. Formation of PhTAD Adducts

Reaction of PhTAD with Acetone

4-Phenyl-1,2,4-triazoline-3,5-Dione (.500g., 2.86 x 10^{-3} mole) was dissolved in 25 ml of acetone (reagent grade) which had been dried overnight over molecular sieves. The resulting bright red solution was allowed to react for 24 hours at room temperature. At the end of this period the now pale yellow solution was dripped into a 10-fold excess of hexane with stirring to give a golden oil which sank to the bottom of the hexane. The hexane was decanted and the oil purified by dissolving in methylene chloride and allowing crystals to grow. These were recrystallized from methylene chloride to give bright yellow, flat diamond shaped

crystals with a melting range of 126° - 127° C. Nuclear magnetic resonance signals were observed at (CDCl$_3$) 2.5 (m,5), 5.6 (s,2), 7.9 (s,3) τ. Mass spectra data indicated the molecular weight to be 233 with major splitting pattern peaks at m/e 191, 190, 177, 119, 91, 77, 57, 43.

<u>Anal.</u> Calcd. for 1:1 adduct $C_{11}H N_3O_3$: C, 56.67; H, 4.71; N, 18.02; O, 20.59.

Found: C, 56.70; H, 4.68; N, 18.11.

<u>Reaction of PhTAD with Allyltrimethylsilane</u>

PhTAD (1.50 g., 8.58 x 10^{-3} mole) was dissolved in 25 ml dichloromethane, to give a bright red solution. This was added dropwise to a solution of allyltrimethylsilane (.978 g., 8.58 x 10^{-3} mole) in 10 ml dichloromethane with stirring. The red PhTAD solution decolorized immediately upon entering the silane solution. The resulting solution was dripped into 350 ml of hexane. Evaporation of the hexane gave a thick oil. This was purified by dissolving in chloroform and adding enough hexane to induce crystallization. Yield, 1.81 g. (73.1%). Nuclear Magnetic resonance signals were observed at (CDCl$_3$) δ 0.18 (s,6), δ 4.20 (d,2), δ 5.33 (m,2), δ 6.0 (m,1), δ 7.46 (m,5). Mass spectral data gives parent peak at 289 with major splitting pattern peaks at: 274, 234, 217, 200, 189, 177, 120, 91, 77, 73, 41.

<u>Anal.</u> Calcd. for 1:1 adduct $C_{14}H_{19}N_3O_2Si$: C, 58.13; H, 6.57; N, 14.52; O, 11.06; Si, 9.71.

Found: C, 58.62; H, 6.43; N, 14.30.

Reaction of PhTAD with Diallyldimethylsilane

PhTAD (1.695 g., 9.69 x 10^{-3} mole) was dissolved in
20 ml of 50/50 acetone/ethyl acetate to give a bright red
solution. A solution of diallyldimethylsilane (.678 g.,
4.85 x 10^{-3} mole) in 10 ml of 50/50 acetone/ethyl acetate
was added dropwise with stirring at room temperature. The
reaction was slightly exothermic. After the addition was
complete, the mixture was still bright red but showed some
cloudiness. After allowing to sit at room temperature for
24 hours, the solution was added dropwise with stirring to
300 ml of hexane to give a viscous orange oil. The oil was
crystallized by grinding in a mortar and pestle with fresh
hexane and drying under vacuum. The resulting fine orange
powder was recrystallized from chloroform. Yield .858 g.
(64.8%). M.P. - Softens at 62° C., Decomposes with evol-
ution of gas at 75° C. Nuclear magnetic resonance signals
were observed at (d_6-acetone) δ 0.28 (m,6); δ 4.30 (m,2);
δ 5.32 (m,1); δ 5.92 (m,1); δ 7.52 (m,5). Molecular weight
from mass spectral data: 273. Splitting pattern peaks at;
230, 217, 200, 189, 177, 160, 153, 139, 132, 120, 119, 100,
91, 83, 77.

Anal. Calcd. for 1:1 adduct, 39, $C_{13}H_{15}N_3O_2Si$: C,
57.13; H, 5.49; N, 15.37; O, 11.70; Si, 10.28.

Found: C, 56.98; H, 6.01; N, 15.44.

Reaction of PhTAD with Diallylmethylphenylsilane

PhTAD (.558 g., 3.19 x 10^{-3} mole) was dissolved in
40 ml of dichloromethane and diallylmethylphenylsilane
(.215 g., 1.06 x 10^{-3} mole) was weighed directly into the
solution. After allowing to sit at room temperature for
24 hours, this was dripped into 400 ml hexane at room
temperature with stirring, to give a white precipitate
which agglomerated on stirring. This precipitate was fil-
tered, washed with hexane and purified by redissolving in
dichloromethane and adjusting the solubility be adding
enough hexane to initiate crystallization. Yield .282 g.
(79.4%). M.P. 94-96° C. Nuclear magnetic resonance sig-
nals were observed at (D_6-acetone): δ 0.52 (m,3); δ 4.20
(m,2); δ 6.20 (m,1); δ 6.62 (m,1); δ 7.45 (m,10). Molecular
weight from mass spectral data; 335. Splitting pattern
peaks at; 322, 293 (very small), 217, 202, 200, 189, 177,
174, 160, 145, 132, 121, 120, 91, 77.

Anal. Calcd. for compound,39,: $C_{18}H_{17}N_3O_2Si$: C,
64.47; H, 5.07; N, 12.52; O, 9.54; Si, 8.38.

Found: C, 64.73; H, 4.97; N, 13.03.

Reaction of PhTAD with Diallyldiphenylsilane

PhTAD (.500 g., 2.86 x 10^{-3} mole) was dissolved in
40 ml of dichloromethane and diallyldiphenylsilane (.377 g.,
1.43 x 10^{-3} mole) was weighed directly into the solution.
After allowing to sit for 24 hours at room temperature,

this was dripped into 400 ml hexane at room temperature
with stirring. This results in a fine white precipitate
which clumps together on stirring. This precipitate was
collected by filtration, washed and purified by redissolving
in dichloromethane and adding hexane to induce crystalliz-
ation. Yield .402 g. (70.9%). M.P. 102 - 103.8° C. Nuc-
lear magnetic resonance signals were observed at (D_6-acetone):
δ 4.26 (m,2); δ 6.35 (m,1); δ 6.72 (m,1); δ 7.38 (m,15).
Molecular weight from mass spectral data: 397. Splitting
pattern peaks at; 355, 277, 236, 224, 217, 177, 120, 119,
105, 91, 77.

Anal. Calcd. for compound, 39,: $C_{23}H_{19}N_3O_2Si$: C,
69.52; H, 4.78; N, 10.57; O, 8.05; Si, 7.07.

Found: C, 69.98; H, 4.39; N, 10.93.

Reaction of PhTAD with Diallylether

PhTAD (1.882 g., 1.07×10^{-2} mole) was dissolved in
30 ml of 50/50 ethyl acetate/acetone to give a bright red
solution. Diallylether (.351 g., 0.35×10^{-2} mole) was
added and the reaction mixture allowed to sit for 24 hours
at room temperature. At the end of this time, the mixture
was still a bright red, but lighter in color than the orig-
inal PhTAD solution. The mixture was dripped into 300 ml
hexane to give a pinkish white powder which was electro-
static on drying. This was purified by recrystallization
from acetone. Yield 1.38 g. (88.2%). M.P. Behavior: De-

composes at 93.4° C. with evolution of gas. Nuclear magnetic resonance signals were observed at (D_6-acetone):
δ 4.22 (m,2); δ 5.00 (m,1); δ 5.82 (m,1); δ 7.36 (m,5);
δ 8.5 (very broad,1). Molecular weight from mass spectral data: 448. Splitting pattern peaks at: 271, 231, 215, 203, 190, 176, 146, 120, 119, 93, 77, 69, 43.

Anal. Calcd. for 2:1 adduct: $C_{20}H_{20}N_6O_5$: C, 58.95; H, 4.46; N, 18.74; O, 17.85.

Found: C, 59.22; H, 4.50; N, 18.94.

REFERENCES CITED

1. J. Thiele and O. Stange, <u>Ann.</u>, <u>283</u>, 1 (1894).

2. R.C. Cookson, S.S.H. Gilani, and I.D.R. Stevens, <u>Tetrahedron Lett.</u>, 615 (1962).

3. B.T. Gillis and J.D. Hagarty, <u>J. Org. Chem.</u>, <u>32</u>, 330 (1967).

4. J. Sauer and B. Schroder, <u>Ber.</u>, <u>100</u>, 678 (1967).

5. F. Yoneda, K. Suzuki, and Y. Nitta, <u>J. Amer. Chem. Soc.</u>, <u>88</u>, 2328 (1967).

6. J.C. Stickler and W.H. Pirkle, <u>J. Org. Chem.</u>, <u>31</u>, 3444 (1966).

7. J.C. Stickler, Ph. D. Dissertation, University of Illinois, 1971, p. 4.

8. A.J. Solo, H.S. Sachdev, and S.S.H. Gilani, <u>J. Org. Chem.</u>, <u>30</u>, 769 (1965).

9. S.S.H. Gilani and D.J. Triggle, <u>J. Org. Chem.</u>, <u>31</u>, 2397 (1966).

10. J. Sauer, <u>Angew. Chem.</u>, (1E) <u>6</u>, 26 (1967).

11. A.B. Evnin, R.D. Miller, G.R. Evanega, <u>Tetrahedron Lett.</u>, 5863 (1968).

12. D.M. Lemal and J.P. Lokensgard, <u>J. Amer. Chem. Soc.</u>, <u>88</u>, 5934 (1966).

13. A.G. Anastassion and R.P. Celluca, <u>Tetrahedron Lett.</u>, 911 (1970).

14. C.M. Anderson, J.B. Bremmer, T.W. McCay, and R.N. Warrener, <u>ibid</u>, 1255 (1968).

15. R. Breslow, J. Hoffman, M. Jacob, Jr., _J. Amer. Chem. Soc._, **94**, 2110 (1972).

16. R.C. Cookson, S.S.H. Gilani and I.D.R. Stevens, _J. Chem. Soc._, 1905 (1967).

17. G.B. Butler, L.J. Guilbault and S.R. Turner, _Polym. Lett._, **9**, 113 (1971).

18. S.R. Turner, L.J. Guilbault and G.B. Butler, _J. Org. Chem._, **36**, 2838 (1971).

19. L.J. Guilbault, S.R. Turner and G.B. Butler, _Polym. Lett._, **10**, 1 (1972).

20. K.B. Wagener, Ph. D. Dissertation, University of Florida, p. 60.

21. D.J. Pasto and A.F.T. Chen, _Tetrahedron Lett._, 2995 (1972).

22. W.H. Pirkle and J.C. Stickler, _Chem. Comm._, 760 (1967).

23. J.K. Stille, _Fortsche. Hochpolymer Forsch._, **3**, 48 (1961).

24. W.J. Bailey, J. Economy and M.E. Hermes, _J. Org. Chem._, **27**, 3295 (1962).

25. J.K. Stille and L. Plummer, _J. Org. Chem._, **26**, 4026 (1961).

26. B. Saville, _J. Amer. Chem. Soc._, **90**, 635 (1971).

27. S.R. Turner, Ph. D. Dissertation, University of Florida, p. 60.

28. K.B. Wagener, Ph. D. Dissertation, University of Florida, p. 53.

29. K.B. Wagener, _ibid._, p. 43.

30. K.B. Wagener, _ibid._, p. 49.

31. Earborn, C. _Organosilicon Compounds_, 1960, Academic Press.

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Wayne Eugene Ruch was born in Pittsburgh, Pennsylvania on November 24, 1946. He graduated from Avonworth High School in June of 1964 and received his Bachelor of Science Degree from the Chemistry Department of Carnegie Institute of Technology in June of 1968. During his senior year of college, he was employed by the Gulf Oil Catalysis Research Group at Mellon Institute.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a master's thesis for the degree of Master of Science.

George B. Butler
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a master's thesis for the degree of Master of Science.

Paul Tarrant
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a master's thesis for the degree of Master of Science.

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